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Application News

LCMS™-8045 and GCMS-TQ™8040

Method for the determination of 313 Residual Pesticides in Black tea using LCMS-8045 and GCMS-TQ8040 NX

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User Benefits

- A modified QuEChERS extraction procedure has been employed for quantifying the pesticides at the desirable concentration levels by using Ultra-fast technologies of LCMS™-8045 and GCMS-TQ™8040 NX.
- Shorter run time of analysis increases the productivity and throughput of the LC-MS/MS and GC-MS/MS system.
- Method employs lower injection volume and lesser flow rate, enhancing column life and stability of assay over longer durations of analysis.

1. Introduction

Tea is one of the most refreshing and aromatic beverage consumed globally. To improve quality and quantity of tea production, broad spectrum of pesticides is frequently applied on its crop. Therefore, Maximum Residual Limits (MRL) are listed by various international regulatory bodies for wide variety of pesticides. Thus, increasing the importance of analytical method for determination of a range of pesticides present in tea.

Based on these requirements, Shimadzu Application Development Center (ADC) has developed and validated a simple, sensitive and high throughput multiclass, multiresidue method for the determination of 313 pesticides in black tea by using LCMS-8045 and GCMS-TQ8040 NX. The multi-residue extraction was performed with modified QuEChERS[1] method for simultaneous quantification of 203 pesticides by LC-MS/MS and 131 pesticides by GC-MS/MS. Out of these, 21 pesticides were common and analyzed by both the techniques. Regulation wise coverage of number of pesticides is shown in Table 1.

Table 1 Coverage of pesticides as per regulations

Compliance / Regulation	No. of compounds regulated	No. of compounds covered in this method
FSSAI	33	19
EU	484	213
APEDA	275	144
JAPAN	230	109

2. Materials and Methods

The reference standards were procured from Restek Corporation with below catalogue numbers:
LC multi residue pesticides kit – 31971
GC multi residue pesticides kit – 32562
Additionally, some individual reference standards were procured from Sigma-Aldrich.
Black tea sample procured from local market, was used to prepare matrix-matched calibration standards and fortified samples. The calibration standards were analyzed in the range of 1 to 50 µg/L for LC-MS/MS and 1 to 15 µg/L for GC-MS/MS. Calibration curves were generated by external standard method and using weighted regression of $1/C^2$. Fortified samples were prepared in six replicates of each 10 and 25 µg/kg for LC-MS/MS and 10 and 20 µg/kg for GC-MS/MS. The compounds marked with asterisk (*) in Table 5; were present in both LCMS and GCMS standard mixture. Hence their calibration curve range and spiking levels were two times the concentration levels mentioned above.

Shimadzu LCMS-8045 with Nexera X2 (Fig. 1) and GCMS-TQ8040 NX (Fig. 2), manufactured by Shimadzu Corporation Japan, were used to quantify residual pesticides in tea sample.

Shimadzu's Method Package Ver.3 for LC-MS/MS and Smart Pesticides Database Ver.2 for GC-MS/MS enabled quick instrumental method optimization for higher throughput. For most of the compounds, 1 target and 2 reference MRM transitions were included in the method.

Shimadzu's data processing software LabSolutions Insight™ was used for data processing, which helped in evaluating validation parameters with ease.

2.1. Sample preparation

The extraction procedure for LC-MS/MS involved modified QuEChERS method. Acidified acetonitrile along with anhydrous magnesium sulphate and sodium chloride were used for extracting pesticides. After extraction, clean up was performed using PSA, C-18, Graphitized Carbon Black (GCB) and anhydrous magnesium sulphate. After clean up, analyte protectant was added to supernatant and subjected to evaporation. and reconstituted ethyl acetate. The final reconstitution volume was adjusted such that fortified samples concentration is diluted by three times.

For GC-MS/MS, acidified ethyl acetate and anhydrous sodium sulphate were used for extraction. After extraction, clean up was performed using PSA, C-18, GCB, calcium dichloride and anhydrous magnesium sulphate. After clean up, supernatant was evaporated and reconstituted ethyl acetate. The final reconstitution volume was adjusted such that fortified samples concentration is diluted by three times.

The extraction and clean up were optimized to maximise recoveries, minimise matrix interference, reduce instrument contamination and achieve lower LOQs.

All samples were analysed as per conditions shown in Table 2 and 3 for LC-MS/MS and GC-MS/MS, respectively.

Fig. 1 Shimadzu LCMS™-8045

Fig.2 Shimadzu GCMS-TQ™8040 NX

2.2. Analytical Conditions

Table 2 Instrument configuration and Analytical Conditions: LC-MS/MS

System Configuration	
LC-MS/MS	: LCMS-8045
Auto-sampler	: Nexera X2 SIL-30AC
Column	: Shim-pack™ XR-ODS II, (150 mm ×3.0 mm I.D. , 2.2 µm)
LC	
Flow rate	: 0.4 mL/min
Mobile phase A	: 2 mM Ammonium formate in water + 0.002% Formic acid
Mobile phase B	: 2 mM Ammonium formate in methanol + 0.002% Formic acid
Gradient program	: 90-10%B (1.0 min to 4.5 min) → 45-55%B (4.5 min to 15.75 min) → 0-100%B (15.75 min to 18.0 min) → 97-3%B (18.0 min to 21.0 min)
Run time	: 21 min
Injection volume	: 10 µL (Co-injection with water)
Column oven temp.	: 40 °C
MS	
Ionization	: ESI
Interface temp.	: 300 °C
Nebulizing gas flow	: 3 L/min
Heating gas flow	: 10 L/min
Drying gas flow	: 10 L/min
DL temp.	: 250 °C
Heating block temp.	: 400 °C

Table 3 Instrument configuration and Analytical Conditions: GC-MS/MS

System Configuration	
GC-MS/MS	: GCMS-TQ8040 NX
Auto-injector	: AOC™-20i + s
Column	: SH-I-5Sil MS (30 m × 0.25 mm I.D., df = 0.25 µm)
Liner	: Topaz Liner, Splitless Single Taper w/Wool
GC	
Injector temp.	: 280 °C
Column oven temp	: 60 °C (1 min), 40 °C/min to 170 °C (0 min), 10 °C/min to 310 °C (7.25 min)
Run time	: 25 min
Injection mode	: Splitless (High pressure at 250 kPa)
Injection volume	: 1 µL
Carrier gas	: He
Linear Velocity	: 36.5 cm/sec (Constant mode)
MS	
Ionization mode	: EI
Ion source temp.	: 230 °C
Interface temp.	: 300 °C
Solvent cut time	: 3.5 min
Loop Time	: 0.5 sec

3. Result and Discussion

Validation parameters like specificity, linearity, recovery and precision were studied as per SANTE guidelines[2]. Results obtained on LC-MS/MS and GC-MS/MS are shown in Table 4 and 5, respectively.

3.1. System precision and specificity

System precision was evaluated by calculating variation of the peak area and retention time of six injections of 10 µg/L pesticide mixture. The %RSD of peak area for 203 compounds on LC-MS/MS and 122 compounds on GC-MS/MS was found to be less than 20%. The retention times' %RSD was within 1 for 203 and 129 compounds on LC-MS/MS and GC-MS/MS, respectively. Specificity of the method was determined by comparing the response of blank sample (reagent and matrix) against reporting level. Response in reagent/matrix blank sample was well within 30% of the reporting limit and met the acceptance criteria.

3.2. Linearity study

For linearity study, matrix-matched calibration standards were used. Calibration curve ranged from 1 to 50 µg/L for LC-MS/MS and 1 to 15 µg/L (2 to 30 µg/L for compounds marked with * in Table 5) for GC-MS/MS. All calibration standards were found within 80 to 120% accuracy as per SANTE guidelines. The linearity graphs of some representative compounds are shown in Figure 3 and 4.

3.3. Recovery study

For LC-MS/MS, fortified samples were spiked with 10 & 25 µg/kg and for GC-MS/MS samples were spiked with 10 & 20 µg/kg (20 & 40 µg/kg for * marked compounds in Table 5). Six replicates of fortified samples were evaluated against matrix-matched calibration curve. Mean recoveries for most of the compounds were found within 70-120%. As per SANTE guidelines, all the compounds were found to be reproducible with 20 %RSD at their LOQ levels.

3.4. Precision study

For precision, repeatability and within-laboratory reproducibility studies were carried out. Concentrations of fortified samples were back calculated against matrix matched linearity.

Repeatability (RSD_r):
Repeatability experiment was performed by injecting six replicates at 10 µg/kg and 25 µg/kg concentration levels in LC-MS/MS and 10 µg/kg and 20 µg/kg in GC-MS/MS. The % RSD for repeatability of six injections at their respective LOQ levels were found to be less than 20%. (Refer to Table 4 and 5)

Reproducibility (RSD_R):
Reproducibility experiment for recoveries was performed on six different fortified samples. The spiked concentration levels were same as mentioned in repeatability study. The % RSD for recovery of six fortified samples at their respective LOQ levels were found to be less than 20%. (Refer to Table 4 and 5)

Table 4 Summary results of LC-MS/MS analysis

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
1	Methamidophos	4.905	142.20>93.95	-15	0.9989	0.010	101.63	59.97	11.74	3.25
2	Formetanate Hydrochloride	4.912	222.00>165.10	-16	0.9910	0.010	98.30	49.20	1.32	1.42
3	Propamocarb	5.134	189.20>102.15	-18	0.9990	0.010	100.83	40.13	5.53	4.21
4	Acephate	5.375	184.00>143.00	-9	0.9935	0.010	101.51	65.54	3.18	1.44
5	Omethoate	5.670	214.10>125.00	-21	0.9986	0.010	101.26	82.27	9.75	2.95
6	Aldicarb Sulfoxide	5.817	207.10>132.15	-9	0.9908	0.010	102.84	53.84	19.21	2.65
7	Dinotefuran	5.881	203.15>114.15	-12	0.9980	0.010	100.76	61.75	14.13	3.11
8	Butoxycarboxim	5.971	240.10>106.15	-14	0.9952	0.010	101.73	111.15	14.29	3.26
9	Aldicarb Sulfone	6.075	240.10>86.20	-23	0.9964	0.010	101.85	106.32	6.14	9.71
10	Methomyl	6.568	163.00>87.90	-10	0.9989	0.010	101.47	101.28	10.23	3.22
11	Thiamethoxam	6.646	292.00>211.10	-13	0.9971	0.010	99.78	76.23	9.35	3.87
12	Dicrotophos	6.918	237.90>72.00	-26	0.9991	0.010	101.02	75.87	6.78	2.63
13	Imidacloprid	7.184	256.10>209.00	-18	0.9981	0.010	101.55	80.80	11.93	2.56
14	Clothianidin	7.301	249.80>169.10	-12	0.9986	0.010	100.25	92.33	12.44	2.51
15	Vamidothion	7.456	288.10>146.05	-13	0.9989	0.010	100.63	87.63	1.37	1.11
16	Carbofuran-3-hydroxy	7.530	255.00>163.15	-19	0.9991	0.010	100.83	92.14	5.83	2.40
17	Mevinphos	7.551	225.10>127.00	-18	0.9994	0.010	100.50	104.19	4.02	3.24
18	Acetamiprid	7.567	223.10>126.10	-22	0.9993	0.010	100.37	99.28	3.12	3.04
19	Dioxacarb	7.670	224.10>123.00	-15	0.9970	0.010	99.74	108.08	12.17	9.00
20	Dimethoate	7.705	230.00>198.90	-9	0.9983	0.010	100.71	100.51	3.34	2.46
21	Fenuron	7.719	165.00>72.15	-17	0.9987	0.010	100.86	91.32	5.39	1.61
22	Trichlorfon	7.768	257.00>109.00	-17	0.9969	0.010	102.10	82.20	11.47	2.31
23	Thiacloprid	7.973	253.00>126.05	-11	0.9975	0.010	100.35	93.28	10.31	3.11
24	Carbendazim	8.156	192.10>160.15	-18	0.9989	0.010	101.20	81.49	13.41	1.38
25	Tricyclazole	8.485	190.00>136.00	-30	0.9992	0.010	100.93	57.39	10.44	0.93
26	Metsulfuron-Methyl	8.701	381.90>167.10	-16	0.9991	0.010	100.55	80.81	1.92	3.13
27	Oxadixyl	8.742	296.20>219.05	-16	0.9935	0.010	100.68	94.93	3.17	3.30
28	Aminocarb	8.823	209.00>137.05	-23	0.9983	0.010	101.05	63.50	3.04	5.65
29	Thiabendazole	8.965	201.80>175.00	-26	0.9978	0.010	101.60	47.56	7.41	4.47
30	Triasulfuron	9.008	401.90>167.00	-19	0.9987	0.010	101.11	89.11	6.95	1.90
31	Carbetamide	9.149	236.90>118.15	-14	0.9996	0.010	100.55	97.17	5.14	1.88
32	Fuberidazole	9.242	184.90>157.15	-24	0.9972	0.010	101.32	77.24	3.42	3.89
33	Thiophanate-methyl	9.427	343.00>151.15	-21	0.9994	0.010	100.92	36.62	7.27	3.35
34	Bendiocarb	9.632	224.10>167.00	-10	0.9992	0.010	100.69	100.09	3.78	1.39
35	Propoxur	9.650	209.90>168.15	-10	0.9982	0.010	101.80	91.04	12.43	2.57
36	Thidiazuron	9.678	221.00>102.00	-17	0.9989	0.010	101.61	80.17	1.56	5.47
37	Carbofuran	9.718	222.10>165.00	-14	0.9990	0.010	100.71	94.95	3.26	2.23
38	Tembotrione	9.746	458.00>341.00	-18	0.9989	0.010	101.00	56.69	8.32	3.63
39	Penoxsulam	9.890	483.90>195.00	-29	0.9975	0.010	101.01	95.74	3.90	1.25
40	Simazine	9.892	202.00>124.10	-20	0.9992	0.010	100.80	84.07	12.75	1.93
41	Metribuzin	9.971	215.10>187.10	-19	0.9952	0.010	102.15	77.80	9.33	3.55
42	Pyracarbolid	10.041	218.10>125.10	-8	0.9984	0.010	101.52	85.69	4.88	4.02
43	Tebuthiuron	10.041	229.10>172.00	-18	0.9992	0.010	100.77	91.32	1.67	2.90
44	Thiodicarb	10.095	354.90>88.00	-18	0.9995	0.010	100.47	96.19	1.54	1.11
45	Carbaryl	10.143	202.10>145.10	-11	0.9989	0.010	100.53	98.85	7.62	2.61
46	Carboxin	10.221	236.10>143.10	-15	0.9993	0.010	101.01	80.69	2.70	1.03
47	Iodosulfuron methyl Sodium	10.299	529.80>163.10	-17	0.9980	0.010	99.25	70.49	7.02	6.61
48	Ethiofencarb	10.547	226.10>107.00	-16	0.9987	0.010	100.98	75.34	2.82	3.70
49	Monolinuron	10.589	215.10>148.00	-13	0.9985	0.010	100.71	87.96	9.92	2.27
50	Diuron	10.602	233.00>72.10	-21	0.9982	0.010	100.95	94.72	4.39	1.89
51	Flumeturon	10.602	233.00>72.15	-22	0.9996	0.010	100.26	98.47	3.82	2.57

Table 4 Summary results of LC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision % RSD_R (n=6)	Precision % RSD_r (n=6)
52	Thiofanox	10.748	241.20>184.00	-12	0.9973	0.010	99.23	88.52	8.51	3.16
53	MCPA	10.863	199.00>141.00	14	0.9989	0.010	100.93	40.12	9.75	3.98
54	Flutriafol	10.884	302.10>70.05	-21	0.9988	0.010	100.05	95.56	5.64	2.53
55	Pirimicarb	10.886	239.20>72.00	-21	0.9992	0.010	101.08	88.18	1.03	1.98
56	Chlorotoluron	10.894	213.10>72.15	-23	0.9976	0.010	100.71	87.97	4.01	1.83
57	Metobromuron	11.061	259.00>170.00	-18	0.9992	0.010	100.68	104.75	4.12	4.56
58	Isoprocarb	11.062	194.10>95.00	-16	0.9993	0.010	100.77	92.93	4.23	1.22
59	Simetryn	11.219	214.10>124.00	-21	0.9987	0.010	101.34	83.44	3.93	1.96
60	Metalaxyl	11.245	280.10>220.00	-15	0.9992	0.010	100.82	94.12	2.58	1.58
61	Halosulfuron-methyl	11.253	434.90>139.00	-47	0.9979	0.010	101.89	92.13	15.50	2.79
62	Methabenzthiazuron	11.303	222.10>150.10	-30	0.9990	0.010	100.76	85.57	7.66	3.65
63	Ethirimol	11.323	210.20>140.20	-22	0.9984	0.010	101.76	48.91	8.81	2.36
64	Isoproturon	11.328	207.20>72.15	-21	0.9986	0.010	100.51	91.79	2.71	1.57
65	Forchlorfenuron	11.358	248.10>129.15	-16	0.9995	0.010	101.13	75.99	7.63	2.92
66	Spiroxamine	11.358	298.20>144.20	-20	0.9990	0.010	101.38	60.81	2.68	1.73
67	Desmedipham	11.588	318.00>136.10	-26	0.9992	0.010	100.79	90.12	1.86	1.55
68	Phenmedipham	11.588	318.10>168.10	-15	0.9985	0.010	101.49	88.64	2.80	2.28
69	Chlorantraniliprole	11.618	483.90>452.90	-19	0.9988	0.010	100.69	92.84	7.32	4.45
70	Cycluron	11.711	199.20>69.10	-23	0.9982	0.010	101.09	81.65	6.83	3.27
71	Azoxystrobin	11.854	404.00>371.95	-5	0.9996	0.010	100.67	93.01	2.02	2.83
72	Furalaxyl	12.106	302.10>95.00	-26	0.9991	0.010	100.56	95.43	2.78	1.65
73	Prometon	12.198	226.20>142.00	-24	0.9995	0.010	100.71	93.41	3.94	1.99
74	Secbumeton	12.198	226.20>142.10	-22	0.9992	0.010	100.63	91.22	1.83	1.75
75	Fenobucarb	12.229	208.10>95.00	-15	0.9993	0.010	100.70	97.77	3.33	2.37
76	Diethofencarb	12.235	268.20>226.05	-10	0.9992	0.010	100.70	92.50	3.13	2.07
77	Ethoxysulfuron	12.252	398.90>261.00	-16	0.9989	0.010	101.17	78.52	3.58	2.86
78	Ethofumesate	12.257	304.10>121.10	-24	0.9966	0.010	102.04	89.75	7.69	1.79
79	Nuarimol	12.312	315.10>251.95	-24	0.9978	0.010	100.94	96.89	8.82	5.56
80	Ethiprole	12.347	397.00>350.90	-21	0.9987	0.010	101.08	90.03	3.69	3.51
81	Methoprotryne	12.378	272.20>197.95	-23	0.9993	0.010	100.70	87.89	3.31	2.47
82	Mandipropamid	12.401	412.10>327.90	-11	0.9981	0.010	100.21	98.29	3.80	2.95
83	Halofenozide	12.403	331.10>275.00	-9	0.9995	0.010	100.51	100.89	11.29	8.93
84	Fenamidone	12.413	312.10>236.00	-16	0.9986	0.010	100.56	91.78	4.08	1.53
85	Siduron	12.455	233.20>94.00	-26	0.9994	0.010	101.05	87.35	6.08	2.74
86	Linuron	12.471	248.80>160.00	-21	0.9979	0.010	100.85	96.00	8.65	2.50
87	Pyrazosulfuron ethyl	12.484	414.90>182.10	-21	0.9996	0.010	100.85	85.91	4.10	2.64
88	Fludioxonil	12.490	247.00>126.15	35	0.9989	0.025	99.11	97.44	5.06	5.62
89	Ametryn	12.538	228.10>186.00	-21	0.9978	0.010	101.10	91.52	2.59	2.80
90	Terbumeton	12.556	226.00>170.10	-18	0.9987	0.010	101.77	89.16	2.35	2.95
91	Methiocarb	12.566	226.10>169.05	-10	0.9986	0.010	100.40	87.35	6.55	2.42
92	Boscalid	12.593	343.00>306.95	-20	0.9980	0.010	100.47	98.40	6.68	3.95
93	Flutolanil	12.657	324.10>261.90	-17	0.9993	0.010	101.05	88.03	4.92	3.70
94	Fomesafen	12.703	456.00>344.00	-15	0.9978	0.025	92.98	90.15	11.56	2.14
95	Methoxyfenozide	12.779	369.20>149.15	-16	0.9972	0.010	101.47	98.44	6.02	1.78
96	Dimethomorph	12.800	388.10>301.00	-21	0.9990	0.010	100.46	90.28	4.30	3.55
97	Paclobutrazol	12.802	294.00>125.05	-37	0.9949	0.010	99.62	93.12	11.87	6.64
98	Promecarb	12.807	208.00>109.10	-16	0.9990	0.010	100.78	94.24	4.32	1.67
99	Pyrimethanil	12.840	200.10>82.00	-24	0.9988	0.010	99.94	86.15	8.81	9.92
100	Mepronil	12.941	270.20>119.05	-26	0.9989	0.010	100.74	92.51	2.29	2.53
101	Mexacarbate	12.969	223.10>166.05	-19	0.9992	0.010	100.53	90.87	2.32	3.87
102	Myclobutanil	13.009	289.10>125.00	-40	0.9994	0.010	101.20	103.69	11.43	5.53

Table 4 Summary results of LC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
103	Triadimefon	13.055	294.10>196.95	-19	0.9982	0.010	100.40	96.37	10.92	4.01
104	Propetamphos	13.086	282.10>138.00	-17	0.9987	0.010	99.77	101.24	13.49	6.03
105	Acibenzolar-S-methyl	13.097	210.90>136.05	-27	0.9995	0.025	84.78	87.13	10.05	3.26
106	Imazalil	13.116	297.10>200.85	-28	0.9959	0.025	102.50	113.89	8.93	5.94
107	Bifenazate	13.154	301.10>170.00	-17	0.9986	0.010	99.83	88.60	7.90	4.78
108	Fluoxastrobin	13.203	458.80>188.10	-35	0.9990	0.010	100.31	92.94	6.32	7.34
109	Butafenacil	13.207	492.10>330.85	-25	0.9987	0.010	100.43	97.14	4.91	3.67
110	Mefenacet	13.218	299.00>148.15	-19	0.9994	0.010	100.26	89.66	4.18	3.06
111	Chloroxuron	13.312	291.10>72.15	-33	0.9986	0.010	100.71	90.00	4.71	2.60
112	Spirotetramat	13.326	374.10>216.00	-39	0.9986	0.010	101.17	85.37	4.64	3.59
113	Triadimenol	13.337	296.10>70.05	-22	0.9989	0.010	100.55	90.92	13.01	1.92
114	Iprovalicarb	13.386	321.20>91.00	-52	0.9987	0.010	99.96	113.67	7.41	3.86
115	Cyproconazole	13.448	292.10>70.05	-34	0.9998	0.010	100.25	90.82	7.22	3.07
116	Tetraconazole	13.449	372.00>159.00	-37	0.9994	0.010	100.89	90.80	12.18	5.38
117	Fluquinconazole	13.462	376.00>349.00	-21	0.9985	0.010	100.97	68.59	15.52	5.65
118	Fenhexamid	13.498	302.10>97.10	-24	0.9968	0.010	100.07	90.15	6.66	3.10
119	Flufenacet	13.529	364.10>152.05	-24	0.9992	0.010	100.11	86.44	1.80	3.07
120	Fenarimol	13.598	331.00>139.10	-39	0.9999	0.010	99.46	107.52	17.70	5.98
121	Triticonazole	13.642	318.10>70.15	-30	0.9997	0.010	100.58	88.76	6.13	4.07
122	Mepanipyrim	13.669	224.10>106.05	-26	0.9985	0.010	101.05	89.36	6.92	3.47
123	Cyazofamid	13.693	325.00>43.95	-36	0.9993	0.010	100.70	91.50	6.30	3.65
124	Prometryne	13.717	242.10>158.00	-29	0.9996	0.010	100.61	86.49	4.13	0.71
125	Terbutryn	13.717	242.10>157.95	-15	0.9996	0.010	100.68	88.77	5.37	3.08
126	Epoxiconazole	13.738	330.00>121.10	-25	0.9986	0.010	101.49	89.75	9.22	4.35
127	Fenoxaprop-P	13.741	332.00>260.00	12	0.9996	0.010	100.87	37.35	18.52	3.63
128	Fenbuconazole	13.779	337.10>125.05	-28	0.9986	0.010	100.04	82.27	14.90	2.94
129	Fipronil	13.855	435.00>330.00	16	0.9972	0.010	100.57	93.18	3.74	2.72
130	Etaconazole	13.863	328.10>159.00	-45	0.9988	0.010	101.15	87.98	12.69	5.88
131	Picoxystrobin	13.947	368.00>145.00	-24	0.9988	0.010	100.52	92.63	2.61	3.81
132	Flusilazole	13.964	316.10>247.00	-16	0.9984	0.010	99.86	84.61	7.90	5.43
133	Tebufenozide	13.972	353.20>133.10	-16	0.9973	0.010	99.71	93.35	3.23	4.75
134	Rotenone	14.010	395.10>213.00	-23	0.9990	0.010	99.47	77.60	14.25	8.92
135	Diflubenzuron	14.023	311.00>158.10	-12	0.9993	0.010	100.43	86.33	6.08	4.37
136	Bupirimate	14.113	317.20>166.00	-21	0.9978	0.010	101.29	83.07	5.86	1.61
137	Clodinafop-Propargyl	14.244	349.90>91.20	-35	0.9995	0.010	100.69	87.28	7.61	2.38
138	Phenthoate	14.266	320.90>247.00	-11	0.9985	0.010	99.75	96.12	2.52	2.68
139	Dimoxystrobin	14.287	327.10>205.00	-8	0.9987	0.010	101.24	90.80	1.31	0.95
140	Iprobenfos	14.287	288.90>91.10	-22	0.9990	0.010	100.87	91.64	2.45	2.63
141	Neburon	14.303	274.80>87.95	-17	0.9988	0.010	100.23	73.24	10.75	1.27
142	Dichlobutrazol	14.392	328.00>70.10	-22	0.9987	0.010	101.00	95.96	6.07	2.63
143	Bromuconazole	14.462	377.90>160.90	-29	0.9953	0.010	100.63	83.61	4.90	4.59
144	Kresoxim methyl	14.462	314.10>267.00	-4	0.9994	0.010	100.07	79.53	9.80	5.22
145	Anilofos	14.485	367.90>198.90	-16	0.9997	0.010	100.52	90.21	3.44	2.92
146	Famoxadone	14.561	391.90>331.25	-10	0.9994	0.010	101.25	95.32	12.05	8.69
147	Tebuconazole	14.584	308.00>70.05	-23	0.9997	0.010	100.90	81.55	9.56	1.10
148	Penconazole	14.585	284.10>70.05	-26	0.9995	0.010	100.97	98.80	8.09	3.15
149	Benalaxyl	14.703	326.20>91.05	-45	0.9996	0.010	100.04	111.54	13.03	2.26
150	Propiconazole	14.822	342.00>158.90	-28	0.9993	0.010	101.24	91.75	9.52	2.11
151	Triflumuron	14.870	359.00>156.05	-20	0.9992	0.010	100.16	78.85	4.02	3.34
152	Pyraclostrobin	14.883	388.00>194.10	-15	0.9993	0.010	100.86	80.18	3.44	3.50
153	Zoxamide	14.892	336.00>186.95	-18	0.9983	0.010	100.31	80.42	3.78	2.89

Table 4 Summary results of LC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision % RSD_R (n=6)	Precision % RSD_r (n=6)
154	Spinosad A	14.898	732.30>142.10	-33	0.9988	0.010	101.12	53.68	3.14	1.69
155	Cyprodinil	14.926	226.10>93.00	-33	0.9981	0.010	101.79	80.39	8.44	2.97
156	Hexaconazole	15.012	314.10>70.00	-35	0.9997	0.010	100.43	78.06	8.56	8.52
157	Baycor (Bitertanol)	15.032	338.00>269.05	-11	0.9996	0.010	100.85	77.46	5.29	5.28
158	Metconazole	15.060	320.10>70.15	-23	0.9991	0.010	100.29	84.16	6.16	2.25
159	Benzoximate	15.106	364.10>198.95	-10	0.9980	0.010	100.06	92.37	6.59	2.44
160	Prochloraz	15.125	376.00>307.95	-8	0.9988	0.010	101.41	73.99	4.73	3.48
161	Indoxacarb	15.259	527.70>150.10	-23	0.9992	0.010	99.45	99.30	4.91	5.15
162	Pencycuron	15.259	329.10>125.00	-10	0.9986	0.010	101.56	70.16	11.27	2.34
163	Clofentezine	15.347	303.00>138.15	-15	0.9985	0.010	101.19	71.38	2.67	3.07
164	Emamectin Benzoate B1a	15.380	886.40>158.10	-41	0.9989	0.010	100.40	54.69	5.88	1.85
165	Hexaflumuron	15.381	458.80>439.00	18	0.9939	0.010	100.10	71.16	15.83	1.07
166	Difenoconazole	15.407	406.10>250.90	-40	0.9985	0.010	101.22	73.74	6.98	3.58
167	Diniconazole	15.411	326.10>70.05	-42	0.9974	0.010	100.70	85.85	7.85	4.66
168	Novaluron	15.422	493.00>141.05	-47	0.9982	0.010	99.69	73.91	10.62	6.81
169	Thiobencarb	15.454	258.10>125.10	-17	0.9993	0.010	100.31	79.92	5.47	2.27
170	Trifloxystrobin	15.456	409.10>145.10	-29	0.9991	0.010	100.88	93.69	7.14	2.73
171	Pyrethrin-II	15.535	373.00>161.00	-12	0.9969	0.010	101.42	88.29	18.13	5.33
172	Clethodim	15.605	360.10>164.15	-25	0.9974	0.010	102.01	71.59	2.29	3.29
173	Spinosad D	15.696	746.40>142.10	-31	0.9989	0.010	101.79	60.85	7.86	3.27
174	Spinetoram A	15.742	748.50>142.20	-31	0.9996	0.010	100.96	53.10	1.47	2.50
175	Triflumizole	15.763	345.90>278.10	-11	0.9988	0.010	100.29	72.29	3.09	3.06
176	Ipconazole	15.786	334.10>70.10	-43	0.9991	0.010	101.16	80.32	8.94	2.51
177	Metaflumizone	15.909	506.80>178.05	-27	0.9987	0.010	99.91	64.12	17.24	8.01
178	Fenoxaprop-Ethyl	16.130	361.90>119.10	-29	0.9975	0.010	102.09	68.79	15.09	3.24
179	Lufenuron	16.209	508.90>339.00	25	0.9969	0.010	98.66	68.08	17.74	8.25
180	Furathiocarb	16.226	383.20>195.00	-44	0.9988	0.010	101.31	88.12	11.93	5.66
181	Fluazinam	16.280	463.00>369.95	30	0.9937	0.025	102.50	68.34	11.82	2.80
182	Tebufenpyrad	16.364	334.20>117.00	-53	0.9993	0.010	100.71	81.95	7.17	2.78
183	Buprofezin	16.476	306.20>201.05	-16	0.9995	0.010	100.55	89.87	6.65	2.81
184	Tolfenpyrad	16.489	384.00>197.10	-26	0.9993	0.010	101.11	74.75	2.93	1.81
185	Teflubenzuron	16.529	379.00>338.90	12	0.9982	0.010	99.66	63.81	10.58	5.13
186	Spinetoram B	16.557	760.60>142.10	-31	0.9976	0.010	101.68	45.42	4.87	1.81
187	Piperonyl butoxide	16.728	356.20>177.00	-26	0.9991	0.010	101.07	88.91	3.40	2.22
188	Fenpropimorph	16.763	304.20>147.10	-27	0.9988	0.010	101.17	70.89	2.39	1.40
189	Flufenoxuron	16.874	489.00>158.10	-21	0.9993	0.010	100.96	53.25	4.53	2.60
190	Pyriproxyfen	16.896	322.10>184.95	-24	0.9987	0.010	101.47	68.00	6.06	1.65
191	Hexythiazox	16.972	353.10>228.00	-20	0.9992	0.010	100.81	67.66	5.36	2.25
192	Spiromesifen	17.007	371.00>273.00	-13	0.9950	0.010	102.20	76.53	17.38	3.13
193	Etoxazole	17.117	360.10>141.10	-17	0.9988	0.010	101.01	68.11	4.36	2.73
194	Propargite	17.128	368.20>231.10	-6	0.9987	0.010	100.62	72.00	3.53	2.23
195	Quinoxyfen	17.205	308.00>197.00	-31	0.9993	0.010	100.84	72.53	9.82	3.16
196	Pyrethrin-I	17.352	329.00>161.10	-11	0.9986	0.010	100.77	71.91	4.64	3.85
197	Spirodiclofen	17.490	411.10>71.10	-35	0.9993	0.010	100.46	74.66	19.98	4.51
198	Fenpyroximate	17.492	422.10>138.10	-30	0.9997	0.010	99.71	67.93	5.80	2.31
199	Pyridaben	18.013	365.20>147.10	-35	0.9990	0.010	101.44	51.14	6.85	3.14
200	Fenazaquin	18.411	307.20>161.10	-26	0.9988	0.010	101.18	51.30	5.08	2.10
201	Doramectin	18.728	916.50>331.15	-27	0.9989	0.010	99.88	92.81	16.30	10.37
202	Etofenprox	19.062	394.00>177.20	-17	0.9976	0.010	102.24	41.37	15.35	4.96
203	Ivermectine	19.374	892.40>569.30	-17	0.9986	0.010	100.55	76.36	7.97	5.55

Table 5 Summary results of GC-MS/MS analysis

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision % RSD_R (n=6)	% RSD_r (n=6)
1	Dichlorvos	4.519	185.00>93.00	14	0.9976	0.01	98.00	86.32	5.74	15.45
2	4-Bromo 2-Chloro Phenol	4.675	208.00>63.00	30	0.9996	0.01	97.00	81.48	7.55	12.97
3	Allidochlor	4.745	132.10>56.00	8	0.9807	0.01	99.00	96.07	10.00	4.87
4	Dichlobenil	5.065	170.90>136.00	14	0.9984	0.01	98.50	90.33	5.36	3.23
5	Biphenyl	5.286	154.10>115.00	24	0.9991	0.01	102.00	92.62	19.18	7.80
6	Mevinphos	5.534	192.00>127.00	12	0.9960	0.01	99.50	94.00	5.25	2.72
7	3,4-Dichloroaniline	5.565	161.00>99.00	22	0.9984	0.01	98.50	88.17	6.34	3.84
8	Etridiazole	5.622	210.90>139.90	22	0.9967	0.02	92.20	49.84	16.71	7.51
9	Pebulate	5.671	161.10>128.10	6	0.9970	0.01	99.00	83.77	12.49	5.89
10	Methacrifos	5.834	208.00>180.00	8	0.9927	0.01	100.50	90.82	8.31	3.47
11	Chloroneb	5.929	193.00>113.00	18	0.9970	0.02	100.00	90.27	6.76	7.36
12	2-Phenylphenol	6.096	170.10>141.10	24	0.9968	0.01	98.00	103.95	16.03	4.70
13	Pentachlorobenzene	6.129	251.90>214.90	22	0.9990	0.01	104.00	68.20	14.89	8.71
14	Tecnazene	6.592	260.90>202.90	14	0.9908	0.01	103.50	70.90	14.59	8.57
15	Propachlor	6.681	120.00>77.00	20	0.9859	0.01	102.50	100.17	13.48	4.48
16	Diphenylamine	6.806	167.10>139.10	28	0.9983	0.02	100.80	79.84	7.17	4.12
17	Ethalfluralin	6.818	276.00>202.00	18	0.9973	0.01	98.00	99.78	16.16	7.61
18	2,3,5,6-Tetrachloroaniline	6.865	230.90>158.00	22	0.9950	0.01	101.50	76.82	9.68	6.58
19	Trifluralin	6.918	264.10>206.10	8	0.9948	0.01	101.50	83.18	15.43	5.27
20	Benfluralin	6.961	292.10>160.00	22	0.9908	0.01	101.50	106.43	10.85	3.58
21	Chlorpropham	6.966	213.10>127.10	14	0.9958	0.01	97.00	83.47	14.58	9.30
22	Sulfotep	7.035	322.00>294.00	4	0.9876	0.02	119.20	67.73	8.05	3.89
23	Di-allate	7.251	234.10>150.00	20	0.9816	0.01	97.00	75.40	17.43	12.40
24	alpha-BHC	7.415	218.90>182.90	8	0.9987	0.01	97.50	64.08	16.06	9.59
25	Hexachlorobenzene	7.500	283.80>213.80	28	0.9905	0.01	100.00	80.02	15.34	8.53
26	Pentachloroanisole	7.555	264.80>236.80	16	0.9944	0.02	103.60	63.01	8.36	8.76
27	Profluralin	7.764	318.10>55.00	22	0.9998	0.01	104.50	62.63	9.41	15.09
28	Clomazone	7.801	204.10>107.00	20	0.9947	0.01	104.50	99.70	9.12	5.55
29	beta-BHC	7.831	180.90>144.90	16	0.9994	0.01	97.00	91.53	19.49	5.30
30	Quintozene	7.866	294.80>236.80	16	0.9569	0.02	90.40	61.68	17.17	13.68
31	Terbufos	7.905	231.00>128.90	26	0.9986	0.01	96.50	83.03	8.23	4.53
32	Phorate	7.906	231.00>129.00	24	0.9946	0.01	100.00	97.32	15.86	3.42
33	gamma-BHC (Lindane)	7.931	180.90>144.90	16	0.9970	0.01	98.00	98.00	17.74	8.46
34	Pentachlorobenzonitrile	7.947	274.80>239.80	18	0.9955	0.02	112.60	79.08	7.73	4.46
35	Terbuthylazine	7.947	229.10>173.10	6	0.9929	0.01	97.50	70.55	19.40	18.33
36	Propyzamide	7.992	172.90>109.00	26	0.9729	0.01	97.50	95.90	5.83	9.88
37	Fonofos	8.017	246.00>137.10	6	0.9984	0.01	99.50	85.85	9.61	5.82
38	Tefluthrin	8.131	177.00>127.10	16	0.9894	0.01	99.50	95.00	6.89	4.51
39	Pyrimethanil*	8.149	198.10>158.10	18	0.9909	0.02	108.40	84.98	11.19	4.84
40	Isazofos	8.180	257.00>162.00	8	0.9968	0.02	104.00	88.30	8.20	9.61
41	Tri-allate	8.314	270.10>186.00	20	0.9933	0.01	103.50	104.87	16.77	11.05
42	delta-BHC	8.398	180.90>144.90	16	0.9988	0.01	99.50	84.65	7.63	8.73
43	Pentachloroaniline	8.674	263.00>192.10	22	0.9966	0.01	98.50	82.22	16.96	7.56
44	Endosulfan ether	8.684	238.90>203.90	16	0.9985	0.02	98.00	93.48	13.87	6.89
45	Dimethachlor	8.764	197.10>148.10	10	0.9983	0.01	95.50	86.27	11.74	4.61

Table 5 Summary results of GC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision % RSD_R (n=6)	% RSD_r (n=6)
46	Acetochlor	8.807	223.10>132.10	22	0.9969	0.02	87.80	88.22	18.84	11.57
47	Chlorpyrifos-methyl	8.834	287.90>93.00	22	0.9918	0.01	95.50	105.67	11.24	4.44
48	Propanil	8.871	217.00>161.00	10	0.9987	0.02	88.00	89.97	10.27	7.26
49	Transfluthrin	8.932	163.10>127.10	6	0.9927	0.02	107.80	82.93	17.60	5.43
50	Parathion-methyl	8.973	125.00>47.00	12	0.9958	0.01	103.00	76.18	14.97	8.57
51	Tolclofos-methyl	8.973	264.90>93.00	24	0.9984	0.01	102.00	85.07	17.46	6.42
52	Alachlor	8.980	188.10>160.10	10	0.9992	0.01	101.50	75.27	12.07	10.87
53	Metalaxyl (Mefenoxam)	9.137	249.20>190.10	8	0.9997	0.01	101.50	80.02	14.99	9.95
54	Fenchlorphos	9.138	284.90>239.90	26	0.9995	0.02	111.80	75.38	17.28	6.33
55	Malathion	9.478	173.10>127.00	6	0.9941	0.02	89.80	81.57	16.28	2.19
56	Dichlofluanid	9.509	223.90>77.00	28	0.9927	0.02	95.60	68.52	15.54	8.00
57	Metolachlor (S-Metolachlor)	9.631	162.00>133.00	16	0.9859	0.01	101.50	106.13	9.42	13.20
58	Chlorthal-dimethyl	9.734	300.90>222.90	26	0.9924	0.02	86.60	86.49	17.73	8.98
59	Triadimefon*	9.857	181.00>127.00	8	0.9938	0.02	105.00	92.05	11.33	6.81
60	Anthraquinone	9.866	180.00>152.00	22	0.9908	0.02	98.00	115.41	18.43	16.33
61	Pirimiphos ethyl	9.943	318.10>166.10	12	0.9997	0.02	90.80	68.84	13.55	8.96
62	Isopropalin	10.047	280.10>238.10	8	0.9986	0.01	96.50	81.42	14.46	4.46
63	Fenson	10.049	141.00>77.00	16	0.9924	0.02	108.40	79.58	8.96	6.71
64	Diphenamid	10.081	239.10>167.10	8	0.9936	0.02	81.40	89.66	14.86	9.05
65	Pendimethalin	10.205	252.10>162.10	10	0.9970	0.01	97.50	98.47	17.23	12.33
66	Cyprodinil*	10.267	224.10>197.10	22	0.9949	0.04	111.60	74.87	17.55	10.46
67	Fipronil*	10.339	366.90>212.90	30	0.9831	0.02	88.20	84.20	11.89	9.33
68	Penconazole*	10.375	248.10>157.10	26	0.9793	0.02	93.20	88.66	9.00	5.10
69	(Z)-Chlorfenvinphos	10.538	267.00>159.00	18	0.9990	0.02	93.00	72.79	12.40	4.46
70	Triadimenol*	10.696	128.10>65.00	22	0.9895	0.02	115.80	78.47	16.91	12.15
71	Bromophos-ethyl	10.739	358.90>302.90	16	0.9977	0.01	100.50	77.62	13.98	14.15
72	o,p'-DDE	10.856	246.00>176.00	30	0.9990	0.01	100.50	79.95	9.98	6.29
73	p,p'-DDE	10.856	246.00>176.00	30	0.9807	0.01	100.50	73.10	9.98	15.12
74	Paclobutrazol*	11.004	236.10>125.00	14	0.9994	0.04	101.20	91.18	7.84	6.36
75	cis-Chlordane	11.080	372.80>263.90	28	0.9984	0.02	103.40	106.68	13.61	7.87
76	Bromfenvinphos	11.166	268.90>161.00	16	0.9984	0.02	90.00	75.40	10.32	9.91
77	Iodofenphos	11.233	376.90>361.80	22	0.9794	0.01	98.00	117.45	14.49	14.80
78	Flutolanil*	11.234	173.00>95.00	26	0.9938	0.02	102.20	79.23	10.97	2.43
79	Prothiofos	11.263	266.90>238.90	10	0.9982	0.02	92.60	87.14	16.41	8.42
80	Chlorfenson	11.266	175.00>111.00	12	0.9959	0.01	99.00	98.23	18.41	2.99
81	Pretilachlor	11.300	238.10>162.10	10	0.9947	0.02	113.40	70.23	12.65	9.84
82	Isoprothiolane	11.350	290.10>204.10	6	0.9969	0.02	105.40	87.37	16.90	7.26
83	Fludioxonil*	11.368	248.00>127.00	26	0.9927	0.02	101.20	86.58	8.36	3.84
84	Myclobutanil*	11.569	179.10>125.00	14	0.9945	0.02	107.20	83.33	10.75	6.18
85	o,p'-DDD	11.571	237.00>199.00	16	0.9967	0.01	95.50	94.03	15.89	6.61
86	Flusilazole*	11.585	206.10>151.10	16	0.9978	0.02	85.60	82.63	28.33	6.29
87	Fluazifop-P-butyl	11.808	383.10>282.10	14	0.9998	0.02	106.40	89.82	15.79	5.22
88	1,1-Dichloro-2,2-bis(4-ethylphenyl)ethane	11.870	223.20>167.10	14	0.9958	0.01	97.00	97.53	16.09	8.85
89	Chlorobenzilate	12.025	251.00>139.00	14	0.9986	0.01	102.00	95.93	12.19	3.58
90	Ethion	12.149	230.90>129.00	24	0.9987	0.01	96.00	103.22	18.61	6.01

Table 5 Summary results of GC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision % RSD_R (n=6)	Precision % RSD_r (n=6)
91	Chlorthiophos	12.202	324.90>268.90	14	0.9951	0.01	101.50	96.45	17.55	4.37
92	p,p'-DDD	12.214	235.00>165.00	24	0.9955	0.01	98.50	103.22	10.12	5.30
93	o,p'-DDT & p,p'-DDT	12.216	235.00>165.00	24	0.9919	0.01	98.50	96.45	10.12	4.27
94	Carfentrazone-ethyl	12.565	340.10>312.10	14	0.9979	0.02	101.40	74.38	14.74	6.08
95	4,4'-methoxychlor olefin	12.644	308.00>238.10	16	0.9950	0.01	100.00	71.62	11.12	8.35
96	Norflurazon	12.803	303.00>145.00	22	0.9950	0.02	92.40	97.58	14.22	17.74
97	Hexazinone	13.118	171.10>71.00	16	0.9998	0.02	104.80	59.83	11.85	7.72
98	Dicofol	13.123	139.00>75.10	28	0.9921	0.01	95.00	102.88	14.40	20.75
99	Propargite-1 & 2	13.133	135.10>107.10	16	0.9948	0.01	102.50	88.80	19.19	13.40
100	Tebuconazole*	13.180	250.10>125.10	22	0.9948	0.02	92.20	85.73	14.06	4.84
101	Diclofop-methyl	13.182	253.00>162.00	22	0.9492	0.01	98.00	94.72	12.54	6.05
102	Piperonyl butoxide*	13.218	176.10>131.10	12	0.9946	0.02	104.20	69.86	16.33	5.42
103	Nitralin	13.257	316.10>274.00	8	0.9911	0.01	103.00	94.72	9.98	18.54
104	Bifenthrin	13.677	181.10>166.10	12	0.9988	0.01	100.50	86.79	9.19	4.64
105	Tetramethrin	13.763	164.00>107.00	14	0.9939	0.01	95.00	85.53	17.03	7.50
106	Phosmet	13.768	160.00>77.00	24	0.9948	0.02	81.80	66.44	16.59	14.62
107	EPN	13.779	169.10>77.00	22	0.9896	0.01	100.00	97.97	14.42	7.22
108	Bromopropylate	13.797	340.90>184.90	20	0.9888	0.01	103.50	98.43	18.81	4.67
109	Fenpropathrin	13.885	265.10>210.10	12	0.9970	0.01	100.50	80.83	18.50	6.18
110	Tebufenpyrad*	13.995	333.10>171.10	20	0.9947	0.02	116.40	84.63	10.53	4.65
111	Tetradifon	14.306	355.90>159.00	18	0.9938	0.01	95.00	86.47	13.77	9.96
112	Leptophos	14.410	376.90>361.90	24	0.9989	0.01	103.00	90.80	18.98	7.24
113	Acrinathrin-2	14.787	289.10>93.00	14	0.9987	0.01	94.50	70.88	16.71	4.96
114	Mirex	14.873	271.80>236.80	18	0.9984	0.01	101.50	86.70	11.84	6.73
115	Fenarimol*	14.966	251.00>111.00	26	0.9917	0.02	96.20	85.82	11.39	3.84
116	Coumaphos	15.665	362.00>109.00	16	0.9988	0.01	100.50	82.66	12.52	7.58
117	Pyridaben*	15.671	364.10>147.10	22	0.9928	0.02	90.40	101.08	10.65	3.18
118	Fluquinconazole*	15.682	340.00>298.00	20	0.9930	0.02	110.40	75.00	4.96	4.39
119	Cyfluthrin-2	16.103	163.10>127.10	6	0.9968	0.01	99.00	88.57	18.82	10.68
120	Cyfluthrin-3 & 4	16.202	163.10>127.10	6	0.9978	0.01	101.50	88.37	14.59	7.48
121	Cypermethrin-1	16.334	163.10>127.10	6	0.9979	0.01	101.50	88.72	14.14	11.12
122	Cypermethrin-2	16.436	163.10>127.10	6	0.9958	0.01	104.00	82.72	11.87	7.22
123	Flucythrinate-1	16.494	157.10>107.10	12	0.9908	0.01	100.00	108.97	8.64	5.10
124	Cypermethrin-3 & 4	16.502	163.10>127.10	6	0.9979	0.01	96.00	72.77	10.96	6.20
125	Etofenprox*	16.654	163.10>135.10	10	0.9973	0.02	100.20	96.85	7.10	4.33
126	Flucythrinate-2	16.686	157.10>107.10	12	0.9963	0.01	98.50	86.77	9.25	3.28
127	Fluridone	17.000	328.00>259.00	24	0.9987	0.01	103.00	107.10	5.69	11.37
128	Fenvalerate-1	17.237	225.10>147.10	10	0.9976	0.02	103.40	83.46	12.59	13.66
129	tau-Fluvalinate-1	17.387	250.10>55.00	18	0.9989	0.01	99.50	81.47	7.49	7.63
130	tau-Fluvalinate-2	17.387	250.10>55.00	18	0.9909	0.01	99.00	87.38	14.34	7.60
131	Fenvalerate-2 (Esfenvalerate)	17.435	225.10>147.10	10	0.9918	0.01	95.50	81.63	13.09	16.69

At LOQ level, out of total compounds, mean recoveries of 169 on LC-MS/MS and 119 on GC-MS/MS were found to be within 70-120%. Whereas 34 compounds on LC-MS/MS and 12 compound on GC-MS/MS showed recoveries less than 70%. As per SANTE guidelines, recoveries of all the compounds were found to be reproducible with less than 20% RSD at their LOQ levels. (Refer to Table 4 and 5)

The method successfully achieved 10 µg /kg LOQ for 198 compounds on LC-MS/MS and 81 compounds on GC-MS/MS. 5 compounds showed LOQ of 25 µg/kg on LC-MS/MS. 48 compounds showed LOQ of 20 µg/kg on GC-MS/MS. Only 2 compounds' LOQ was found to be 40 µg/kg (Refer to Table 4 and5). Representative chromatograms of few compounds at their LOQ levels are shown in Figure 3 and 4.

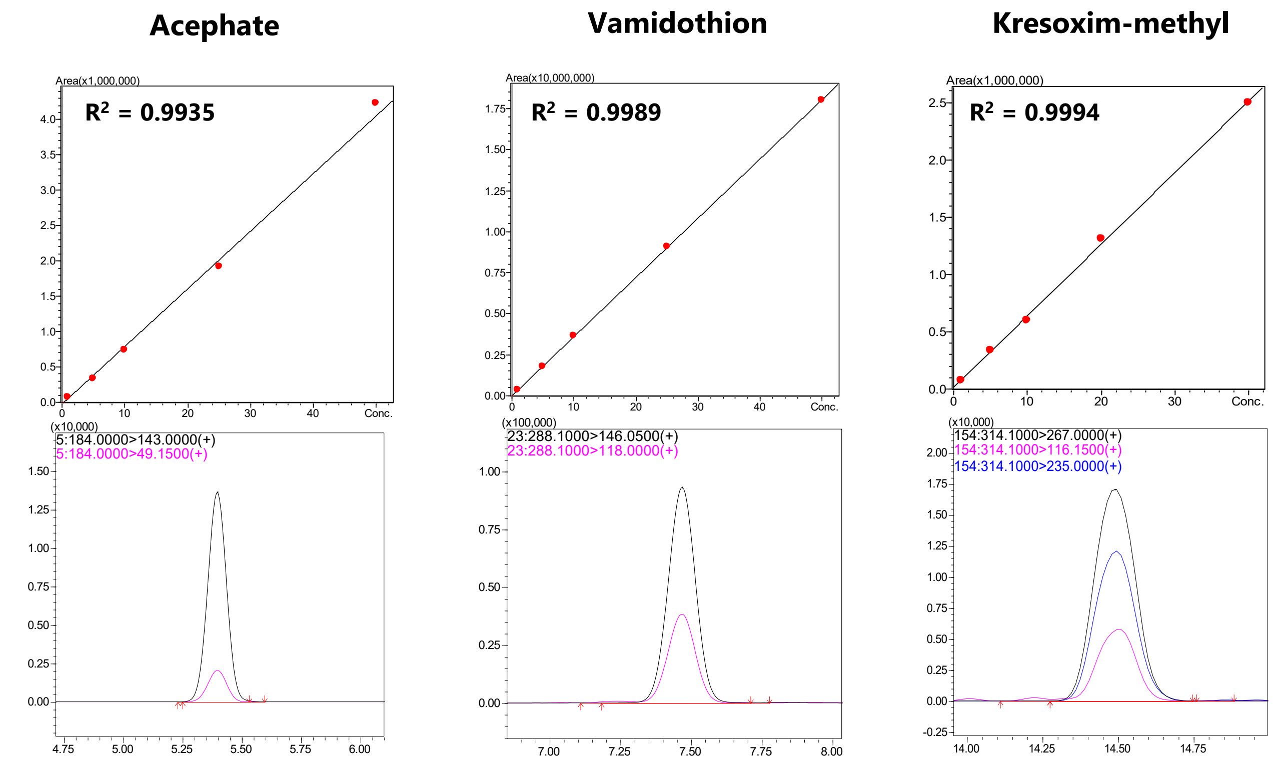

Fig. 3 Representative linearity graphs and chromatograms at LOQ level for LC-MS/MS compounds

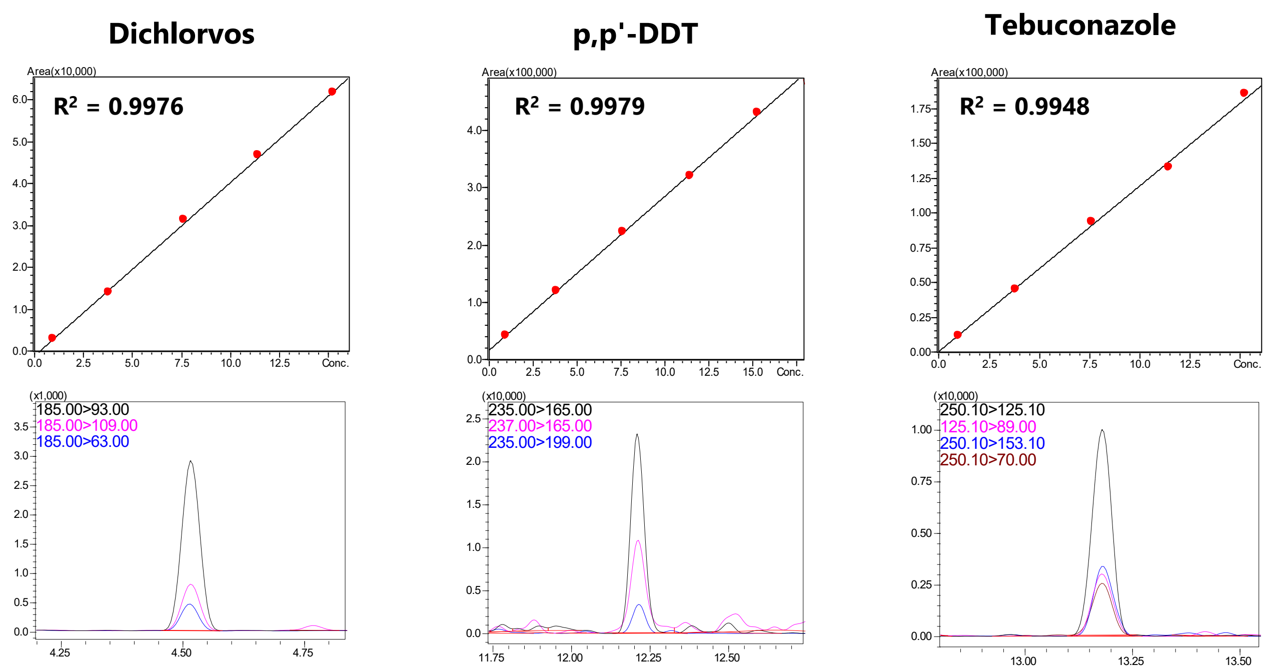

Fig. 4 Representative linearity graphs and chromatograms at LOQ level for GC-MS/MS compounds

4. Conclusion

A simple, sensitive and rapid method has been developed to quantify 313 pesticides by LC-MS/MS and GC-MS/MS in tea sample. Quantification of pesticides in black tea is challenging due to the complexity of matrix. Hence, a modified QuEChERS extraction technique was used for sample preparation.

The method developed on Shimadzu LC-MS/MS and GC-MS/MS proved to be highly sensitive and reproducible as most of the compounds showed good RSD_r and RSD_R (as per SANTE guidelines) at trace levels.

This highlights the reliability of the method and enables its use in testing laboratories for multi-residue analysis of tea samples.

5. References

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